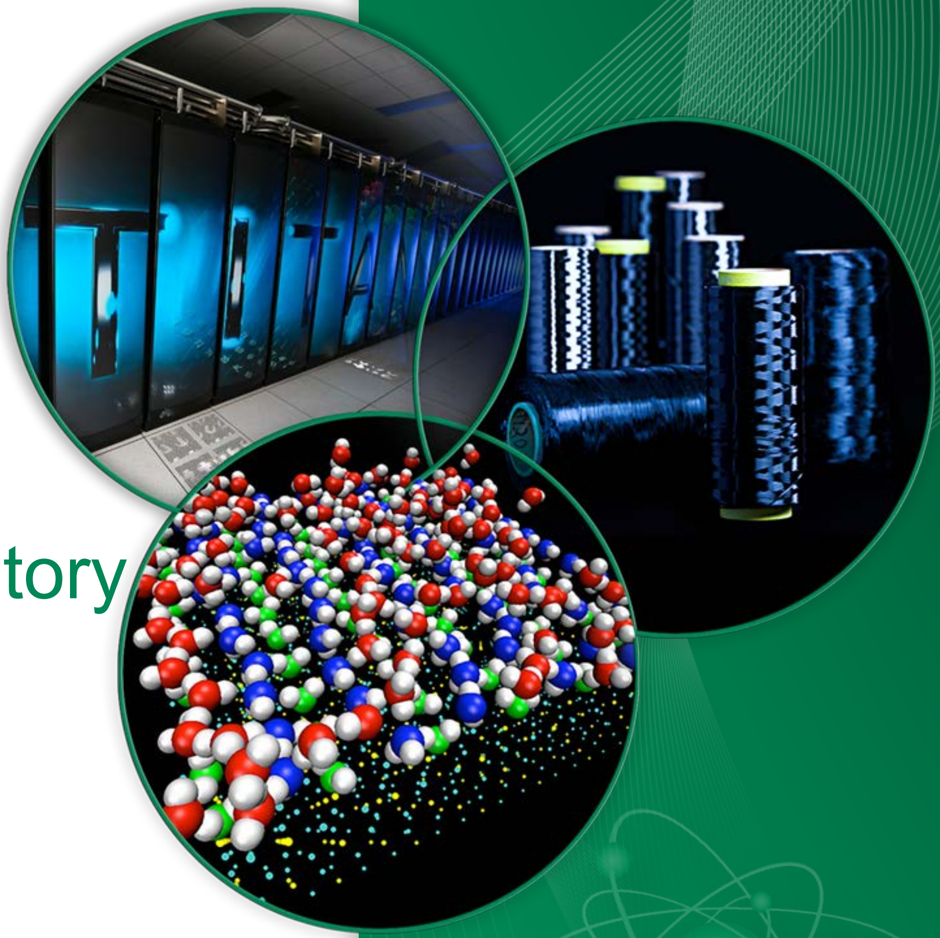
Thermoelectrics Theory and Structure



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PM013

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Overview

Timeline

- Started FY09.
- Completion FY14.
- 75% Complete.

Budget

- Total project funding.
- 100% DOE.
- FY12: $375K.
- FY13: $340K (anticipated).
- FY14 $340K (anticipated)

Barriers*

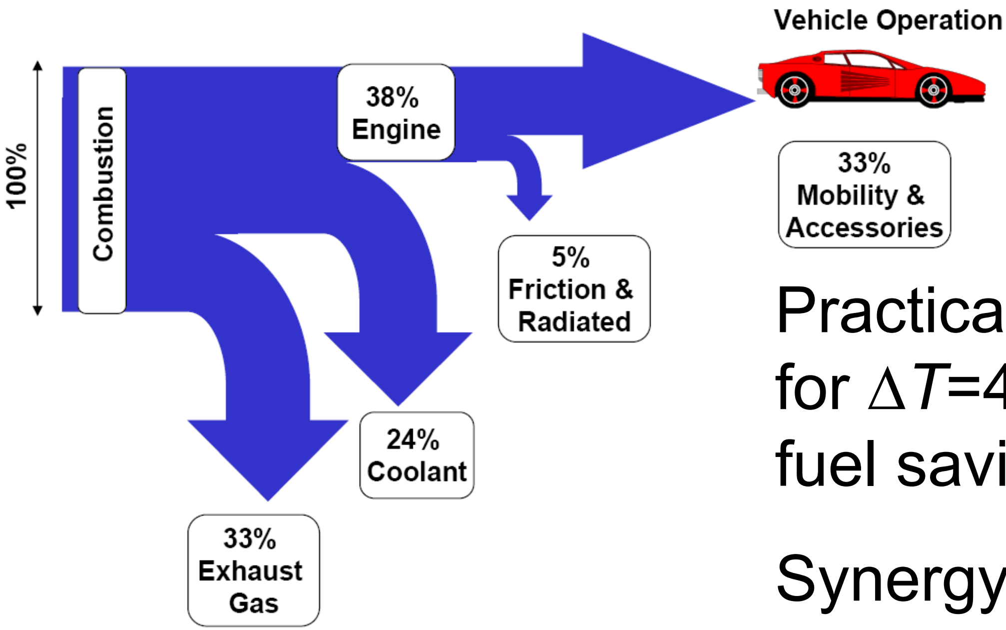
- Need high *ZT* for waste heat recovery (*ZT*>2) for 10% fuel savings.
- Need cost effective materials (target $1/Watt, desirable $0.2).
- Need durable *p*- & *n*-type materials.
- Need materials without rare elements, e.g. Te.

Partners

- Interactions/ collaborations:
  - Massachusetts Institute of Technology (S^{3}TEC Center)
  - General Motors
  - Ford Motor Co.
  - University of Washington
  - Naval Research Laboratory
  - University of Houston
- Project lead: ORNL

* DOE Vehicle Technologies Multi-Year Program Plan 2011-2015, Solid State Energy Conversion 2.3-4 and 2.3-5; Propulsion Materials Technology 2.5-3, Task 2 (Materials for Exhaust Systems and Energy Recovery) and Task 4 (Materials-by-Design).

Relevance



$$ZT = \sigma S^2 T/\kappa$$

Exhaust and EGR loop gas have potential for substantial energy recovery.

Practical materials with $ZT > 2$ for ΔT=400 +/- 50 C can yield fuel savings of 10%. [1,2]

Synergy with truck electrification.

Efforts at General Motors, Ford, Toyota/Denso, BMW, Volkswagen, Bosch, Amerigon/BSST, Siemens, Cummins …

[1] DOE Vehicle Technologies Program Plan 2011-2015
[2] "Science Based Approach to Development of Thermoelectric Materials for Transportation Applications: A Research Roadmap", DOE FCVT (2007).

2.3.2 Solid State Energy Conversion

Goals

The goal of the Solid State Energy Conversion activity is to develop advanced thermoelectric technologies for recovering engine waste heat and converting it to useful energy that will help improve overall engine thermal efficiency to 55 percent for Class 7 and 8 trucks, and 45 percent for passenger vehicles while reducing emissions to near-zero levels. More specifically,

- By 2015, achieve at least a 17 percent on-highway efficiency of directly converting engine waste heat to electricity which will increase passenger and commercial vehicle fuel economy by 10 percent.
- By 2015, reduce by at least 30 percent, the fuel use to maintain occupant comfort through the use of thermoelectric heaters/air conditioner (TE HVAC) systems.

This activity also supports the overall engine efficiency goals of the FreedomCAR and Fuel Partnership, and 21st CTP. The technical targets for Solid State Energy Conversion are shown in Table 2.3-4.

Significant effort, and promising preliminary results, on thermoelectric materials for vehicle climate control (see Accomplishments)

Relevance

Barriers:

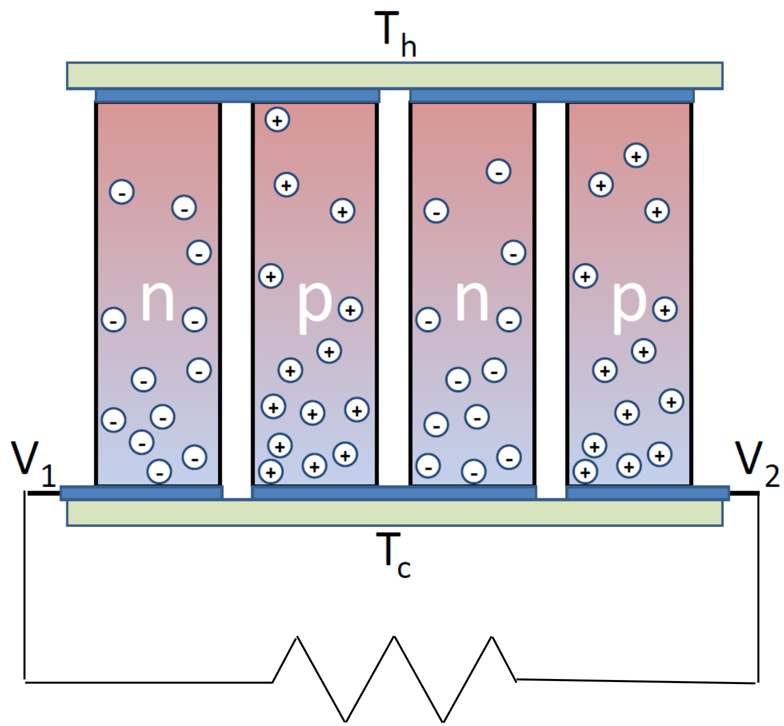
•Need high *ZT* (ideally *ZT*=2 or higher for waste heat recovery, ZT >1 for climate control).

•Need low cost ($1/watt or better).

•Need *p*-type and *n*-type.

•Need high availability, manufacturable materials – concern with Te: low abundance, solar cell use.

•Avoid materials with toxic components.



Thermoelectric generator

To save energy a technology must not only work – it must be used.

Thermoelectrics Theory and Structure

- Find promising thermoelectric compositions for waste heat recovery in vehicles (waste heat → electrical power).
- Focus on inexpensive materials that can be used.
- Use science based approach especially materials design strategies based on first principles.
- Potential additional benefit: Improved materials for climate control systems → Impact on Electric Vehicles.

Identify trends / strategies /design rules

Compositions/Collaborations w/Expt.

FY10 FY11 FY12 FY13 FY14

Milestones

3/31/2013: ***Identify a low cost material with high thermopower from 300 to 600 Celsius and other properties suggesting high performance for waste heat recovery. Document this in a technical report describing the scientific basis for this identification***.

We examined the potential thermoelectric performance of a number of materials by calculating essential quantities such as the n- and T-dependent Seebeck coefficient and the electrical conductivity anisotropy.

We down-selected three low cost materials, $CrSi_2$, CoSbS, and p-type Mg_2Si. Found each has potential for high performance at above temperatures. Collaborated with experimental study on CoSbS. Published three technical reports documenting these findings.

Technical Reports:

D. Parker, A.F. May, H. Wang, M. A. McGuire, B.C. Sales and D. J. Singh, *Phys. Rev. B* **87**, 045205 (2013); D. Parker and D.J. Singh, *New J. Phys*. **14**, 033045 (2012); J.J. Pulikkotil, D.J. Singh, S. Auluck, M. Saravannan, D.K. Misra, A. Dhar and R.C. Budhani, *Physical Review B* **86**, 155204 (2012).

Milestones

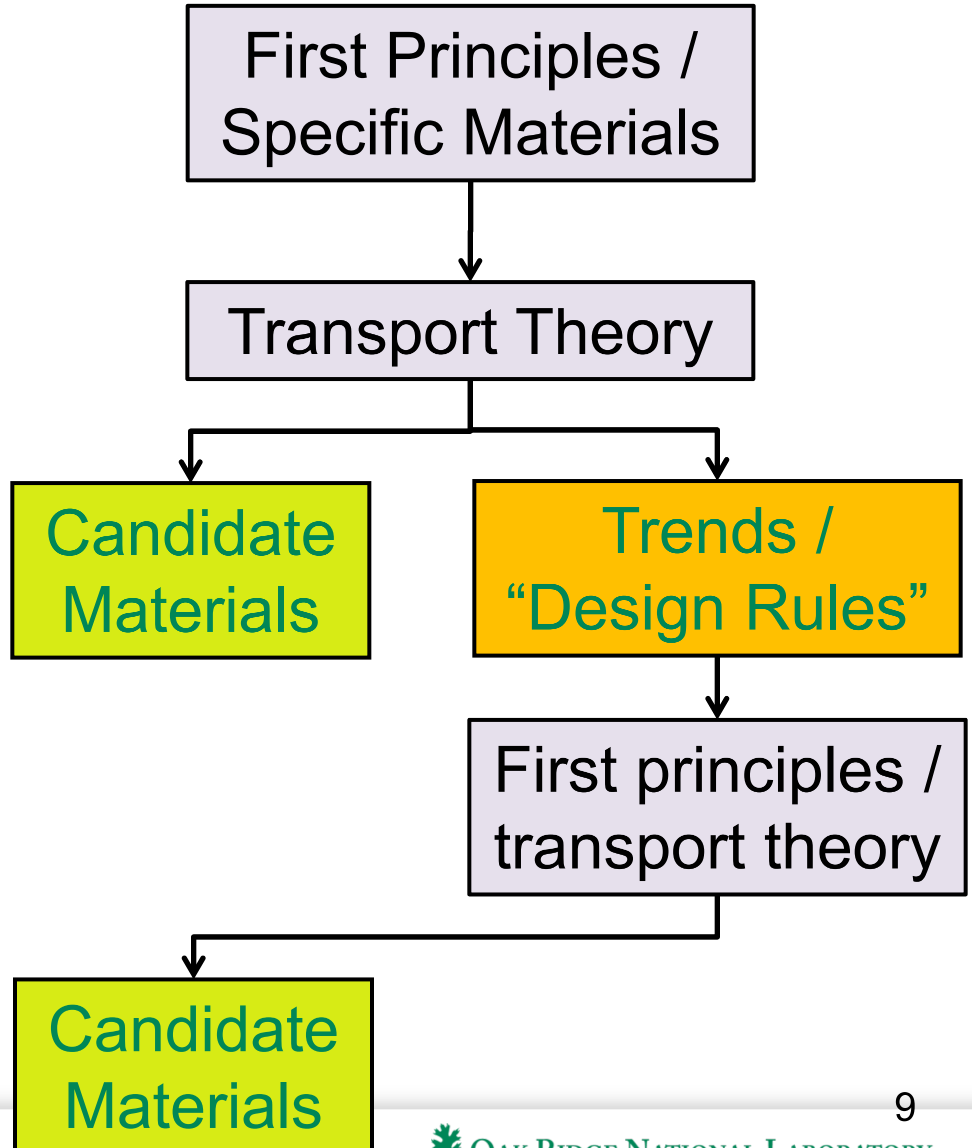
9/31/2013: ***Perform detailed calculations of the doping level dependent thermoelectric properties for two materials that are promising for room temperature application, identify the optimum carrier concentration, and document in a technical report.***

We have identified two such materials: Ca_2Pb and Ba_2Pb – both comprised of low cost elements.

Theoretical calculations indicate that both these materials may have substantial thermopower values in a temperature range suitable for ambient temperature heating and cooling applications. Presently identifying optimal doping levels.

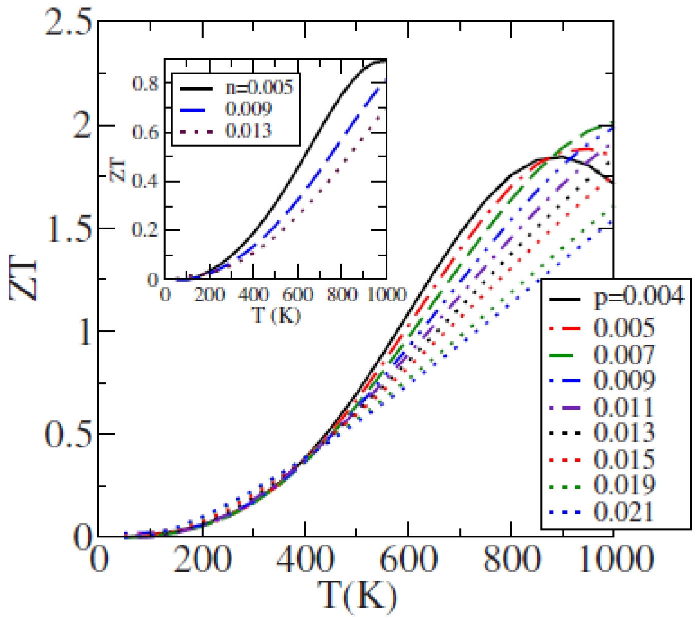
Approach/Strategy

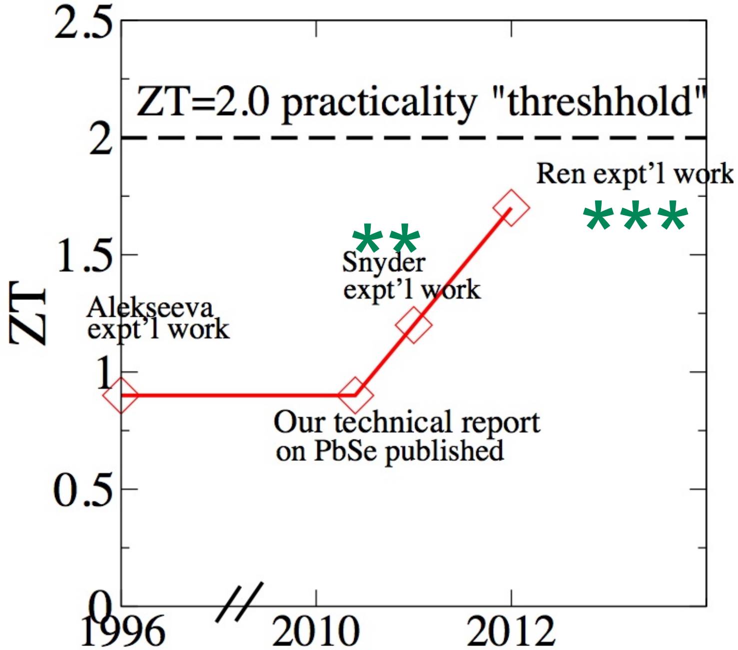
- First principles calculations.
- Transport theory ➔ electrical transport quantities (T and n-dependent Seebeck coefficient, conductivity anisotropy).
  - ORNL developed BoltzTraP code.
  - Materials-by-Design type approaches to accelerate materials discovery.
- Focus on materials that promise potential low cost.
- Experimental collaboration for testing, synthesis
- Complementary to ORNL project on mechanical properties related to packaging / devices (Wereszczak).



Approach – Predictive

PbSe: potential high performance thermoelectric, overlooked until our prediction* of p-type ZT as high as 2 at 1000 K, 1.7 at 800 K.





1.7 800 K ZT confirmed

N-type ZT of 1.3 found by Ren+ (our calculations find this also).

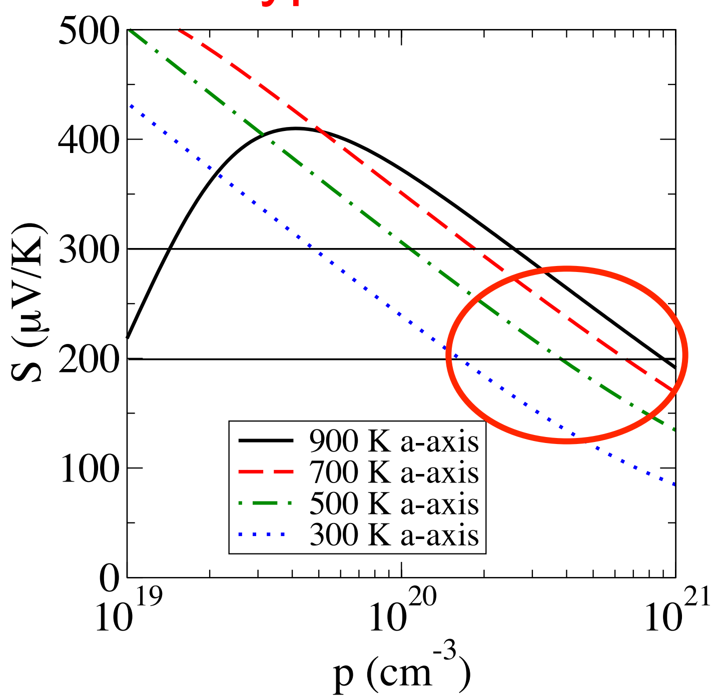
*D. Parker and D.J. Singh, Phys. Rev B **82**, 035204 (2010)

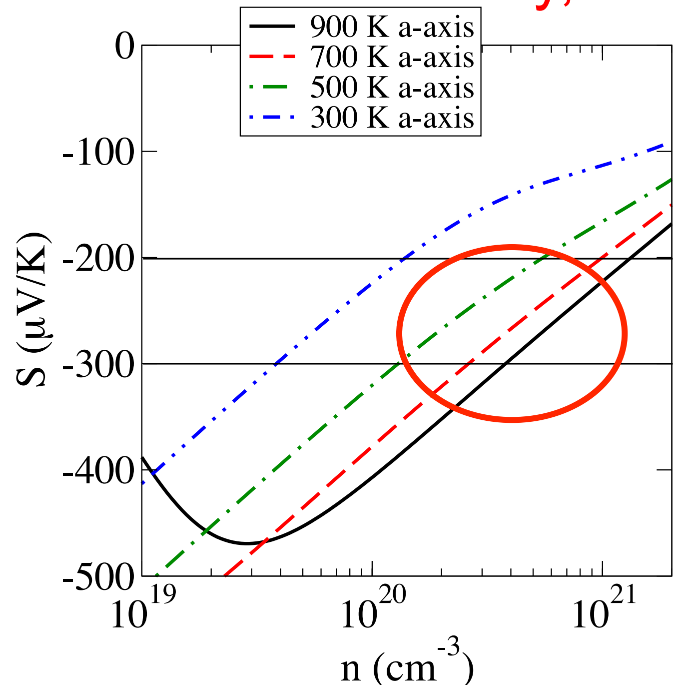
Y. Pei et al, Adv. Mat. **23, 1367 (2011); ***Q. Zhang et al, J. Am. Chem. Soc. **134**, 10031 (2012); +Q. Zhang et al, Energy and Env. Sci **5**, 5246 (2012)

Current Year Accomplishments – CoSbS

- Detailed band structure and transport calculations (thermopower).
- ORNL experimental work (M. McGuire) confirming predictions.
- Preparation and publication of a detailed technical report*.

Note high thermopower at heavy doping for both p and n-type – favorable for electrical conductivity, ZT



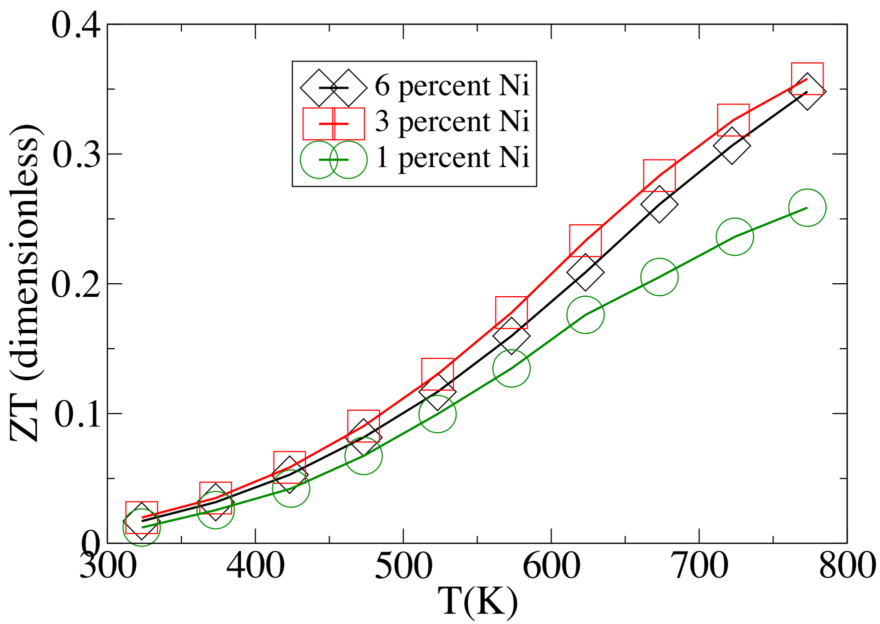


*D. Parker, A.F. May, H. Wang, M. A. McGuire, B.C. Sales and D. J. Singh, Phys. Rev. B **87**, 045205 (2013).

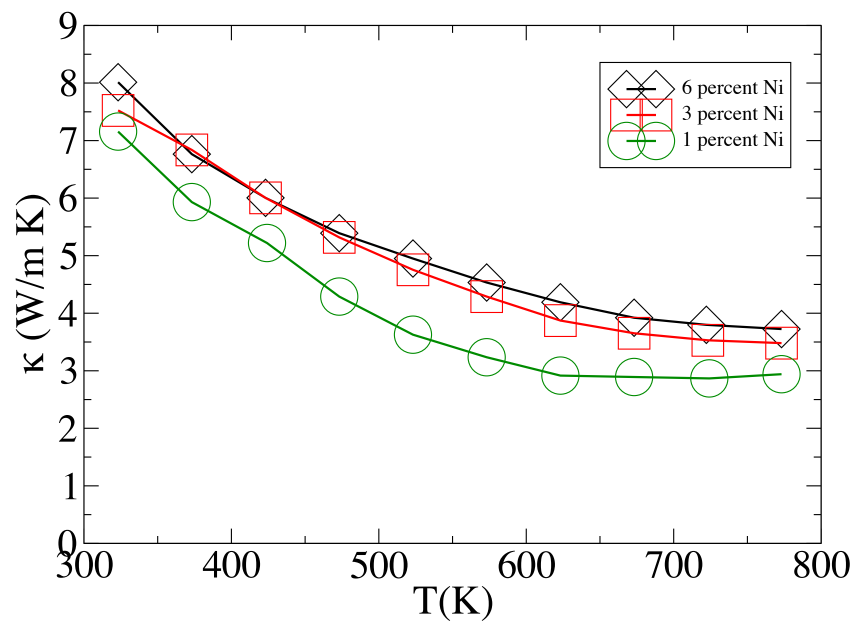
Current Year Accomplishments – CoSbS

Promising N-type ZT of 0.35 found experimentally at 773 K; only first study of this material and optimization of doping/alloying/ nanostructuring expected to raise ZT above unity.

Lattice thermal conductivity is fairly high (7 W/m-K @ 300 K) and suggests that thermal conductivity reduction will yield large performance enhancements.



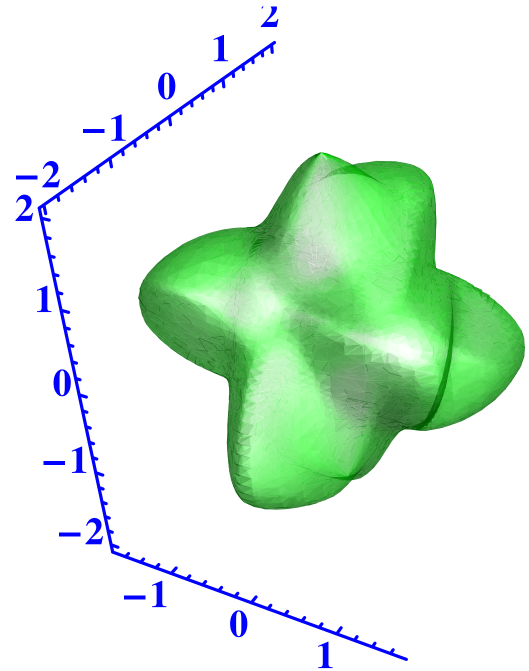
ZT Values



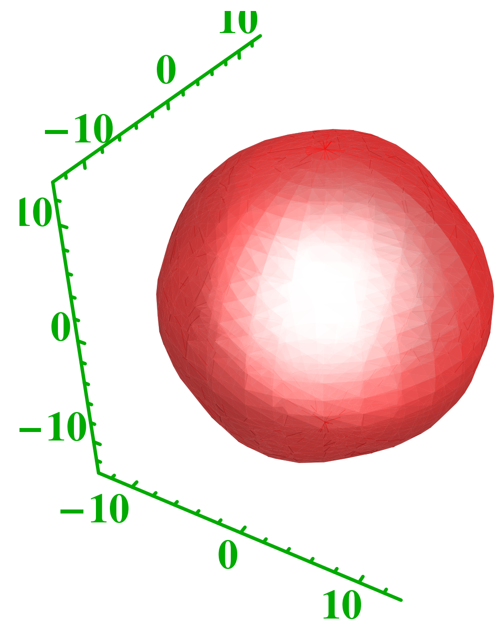
Thermal conductivity

Current Year Accomplishments – Acoustic Impedance Mismatch Scattering

- Identified sound speed anisotropy, leading to acoustic impedance mismatch in randomly oriented granular sample, as key factor in reduction of thermal conductivity by nanostructuring.
- Published technical report documenting this finding.*



Bi_2Te_3 sound speed anisotropy (km/sec)



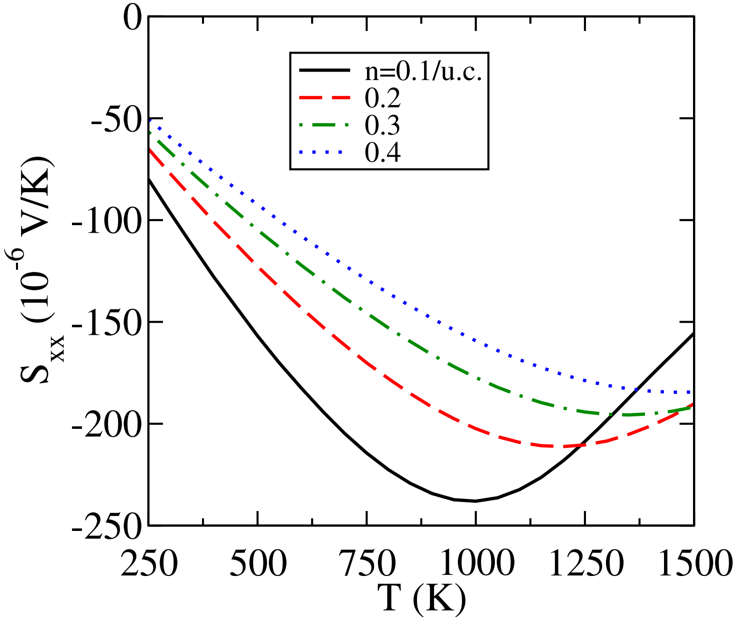
Diamond sound velocity anisotropy

*X. Chen, D. Parker and D.J. Singh, *Phys. Rev. B* **87**, 045317 (2013).

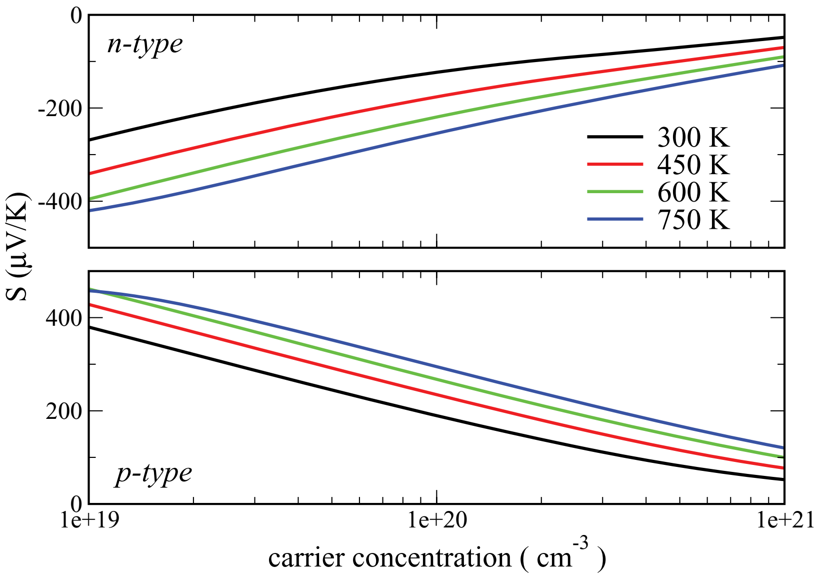
Current Year Accomplishments – Silicides $CrSi_2$ and Mg_2Si

Need inexpensive n-type materials for waste heat recovery (much of previous work on e.g. PbTe/PbSe where p-type is best). Studied (published* in open access journal) n-type $CrSi_2$.

Also beneficial to have isotropic, low-cost p-type material. Studied and published technical report** on cubic Mg_2Si.



Planar thermopower for $CrSi_2$



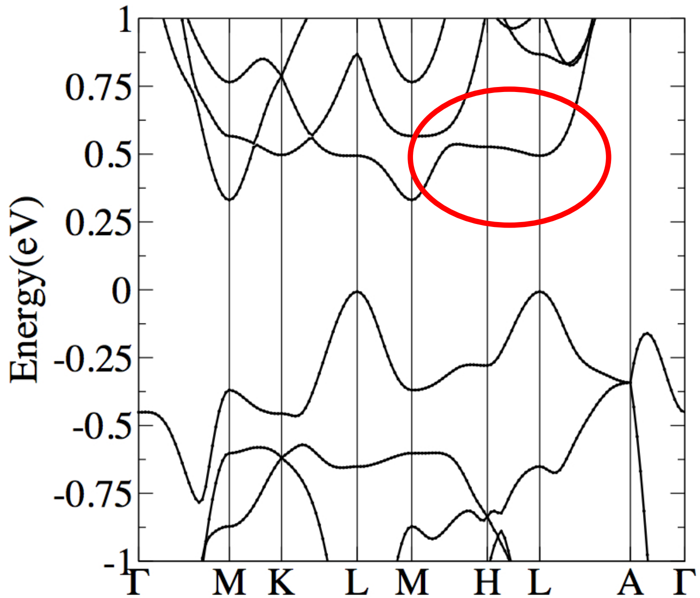
Thermopower for Mg_2Si

*D. Parker and D.J. Singh, New J. Phys. **14**, 033045 (2012).

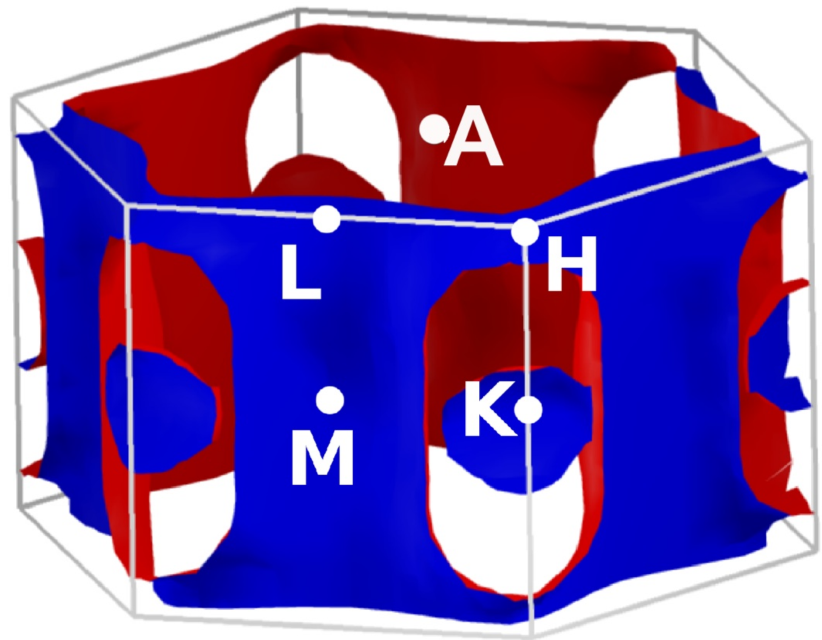
J.J. Pulikkotil, D.J. Singh, S. Auluck, M. Saravannan, D.K. Misra, A. Dhar and R.C. Budhani, Physical Review B **86, 155204 (2012).

Current Year Accomplishments – $CrSi_2$

Favorable n-type thermopower due to heavy-band, low dimensional electronic structure – useful design principle.



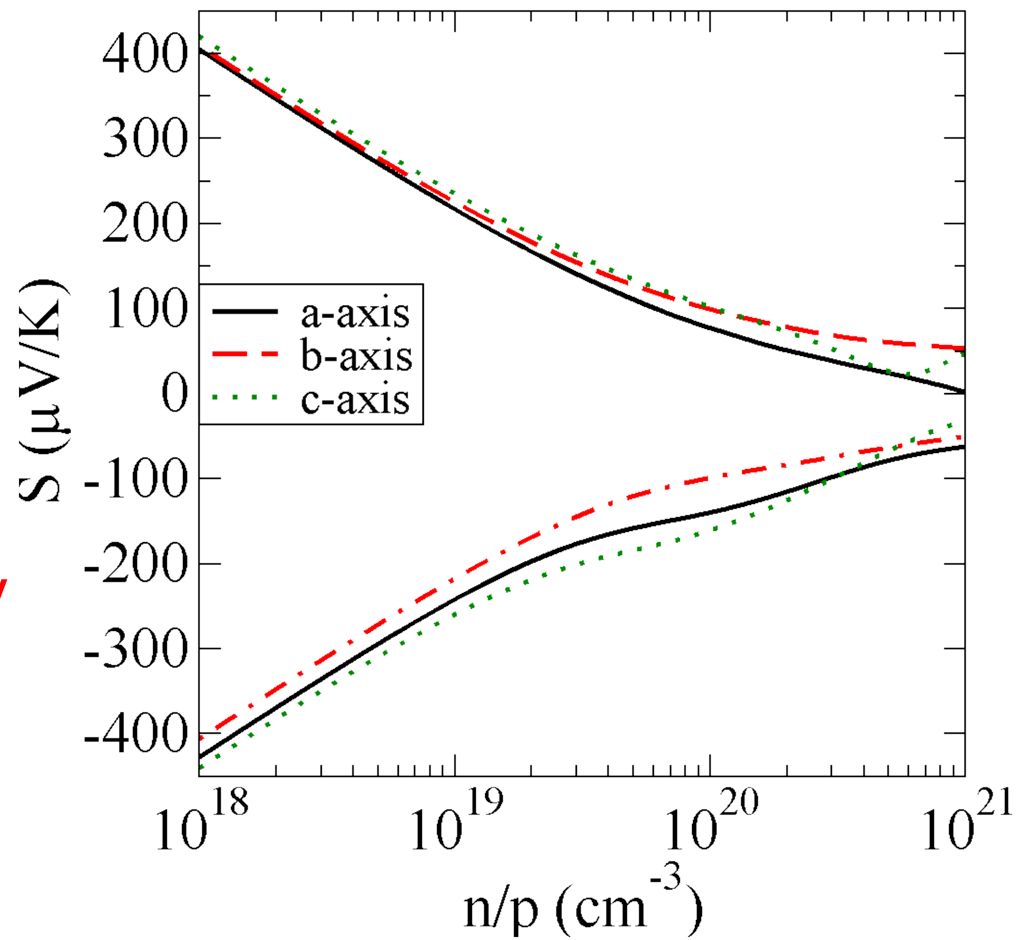
$CrSi_2$ band structure, note heavy band



Fermi surface for doping n=0.3/u.c. (2.8×10^{21} cm^{-3})

Preliminary Results: Ca_2Pb for Heating/Cooling Applications

Ca_2Pb noted to have significant room-temperature ZT (0.2) in 1962*, little study since then. Performed thermopower calculations on this material, appears favorable both p-type and n-type. Optimization likely to yield substantial improvement over 1962 work.



*V.A. Russell and P.H. Klein, Adv. Energy Conv. **1**, 147 (1962)

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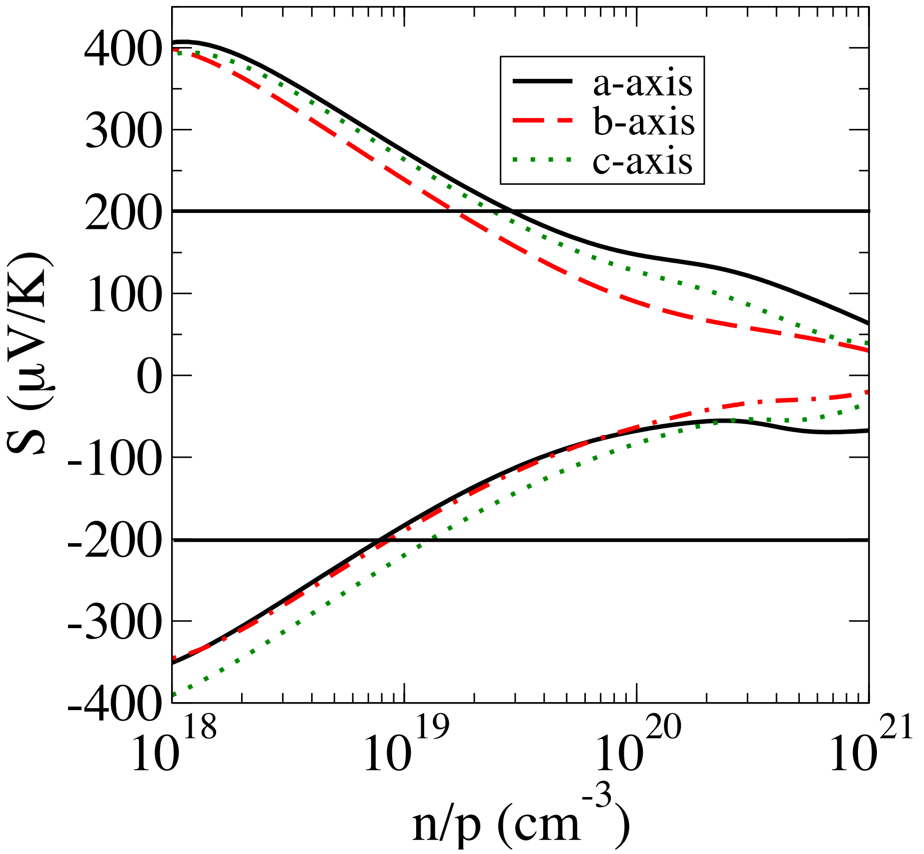
Preliminary Results: Ba_2Pb

300 K thermopower similar to Ca_2Pb, likely lower lattice thermal conductivity due to heavier element Ba.

Favorable for both n-type and p-type, important for applications (avoid thermal expansion problems).



Collaborations

- Massachusetts Institute of Technology

  S^{3}TEC center - thermoelectric power generation technology.

  MIT very synthesis oriented → good avenue for transitioning results.

  Discussions/communications – especially low cost skutterudites, vehicular heating/cooling applications.
- General Motors

  Discussions/communications – especially low cost skutterudites, vehicular heating/cooling applications.
- Ford

  Discussions/communications – vehicular heating/cooling applications.
- University of Washington

  Collaboration on publication studying transport in p-type skutterudites.
- Naval Research Laboratory

  Discussions/communications – thermal conductivity.
- University of Houston

  Discussions/communications – thermoelectrics for waste heat recovery.

Preliminary Result and Proposed Future Work – FY14

- **Preliminary result**: Ca_2Pb, Ba_2Pb potentially useful room-temperature and high temperature thermoelectrics.
- **Proposed Future Work**:
    1. Determine optimal doping levels for above materials and prepare technical report for submission.
    2. Study (via Boltzmann transport and lattice dynamics calculations) low cost families of potential thermoelectric materials – focus on Te-free materials with heavy mass bands, soft phonons and other properties indicative of thermoelectric performance.

Summary

- **Relevance:** Project addresses key exhaust waste heat recovery barriers: (1) materials performance, (2) need for *p*-type and *n*-type material, (3) need for low cost materials → *overcoming these barriers can yield 10% fuel savings*. Project also impacts climate control – *EV-enabler* - similar barriers but need room temperature performance.
- **Approach/Strategy:** Perform first principles calculations to guide selection and optimization of thermoelectric materials.
- **Accomplishments:** Published technical reports on Mg_2Si, CoSbS and $CrSi_2$, low cost thermoelectric materials for use in exhaust waste heat recovery. Published technical report identifying acoustic impedance mismatch scattering as agent for thermal conductivity reduction in nanostructured thermoelectrics.
- **Collaborations:** GM, Ford, MIT, Nav. Res. Lab., U. Wash., U. Houston.
- **Proposed Future Work:** Identify low cost thermoelectric materials potentially useful for room temperature heating/cooling applications and waste heat recovery. Determine optimal doping regimes for Ca_2Pb and Ba_2Pb.